

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C07D 487/04, A01N 43/90 // (C07D 487/04, 249:00, 239:00)</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/46607</b> <b>(43) International Publication Date:</b> 22 October 1998 (22.10.98)
<b>(21) International Application Number:</b> PCT/US98/05614 <b>(22) International Filing Date:</b> 23 March 1998 (23.03.98) <b>(30) Priority Data:</b> 08/843,322 14 April 1997 (14.04.97) US <b>(71) Applicant:</b> AMERICAN CYANAMID COMPANY [US/US]; Five Giralda Farms, Madison, NJ 07940 (US). <b>(72) Inventors:</b> PEES, Klaus-Jürgen; Soonwaldstrasse 9, D-55129 Mainz (DE). ALBERT, Guido; Volxheimer Strasse 4, D-55546 Hackenheim (DE). <b>(74) Agents:</b> MAZZARESE, Joseph, M.; American Home Products Corporation, Patent Law Dept. - 2B2, One Campus Drive, Parsippany, NJ 07054 (US) et al.		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> FUNGICIDAL TRIFLUOROPHENYL-TRIAZOLOPYRIMIDINES  <b>(57) Abstract</b>  The novel compounds of formula (I) (R <sup>1</sup> , R <sup>2</sup> and Hal are defined in the specification) show selective fungicidal activity. The new compounds are processed with carriers and adjuvants to fungicidal compositions. <div data-bbox="673 1134 1266 1386"><p style="text-align: right;">(I)</p></div>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

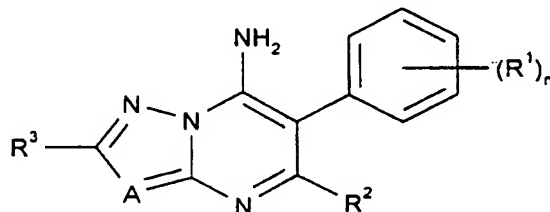
AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## FUNGICIDAL TRIFLUOROPHENYL-TRIAZOLOPYRIMIDINES

### BACKGROUND OF THE INVENTION

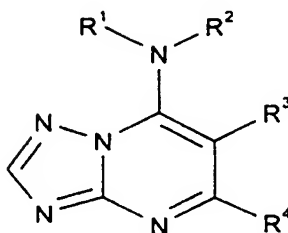
This invention relates to certain triazolopyrimidine compounds, a process for their preparation, compositions containing such compounds, a method for combating a fungus at a locus comprising treating the locus  
5 with such compounds and their use as fungicides.

EP-A-0071792 claims compounds of the general formula



in which R<sup>1</sup> represents alkyl, halogen, alkoxy, cyano, cycloalkyl, aryl, aryloxy, arylthio, aralkyl, arylthio, arylalkyl, arylalkyloxy or arylalkylthio  
10 each optionally substituted by halogen or alkoxy; or (R<sup>1</sup>)<sub>n</sub> represents a benzene, indane or tetrahydronaphthalene ring fused with the phenyl ring, aromatic moieties in the above groups being optionally substituted by alkyl, alkoxy, halogen or cyano; n is 1 or 2; R<sup>2</sup> and R<sup>3</sup> are each hydrogen, alkyl or aryl, A represents a nitrogen atom or a CR<sup>4</sup> group, and R<sup>4</sup> is as R<sup>2</sup>  
15 but can also be halogen, cyano or alkoxycarbonyl or together with R<sup>3</sup> can form an alkylene chain containing up to two double bonds. The compounds are said to be active against various phytopathogenic fungi, especially those of the phycomycete class. However evidence of fungicidal activity is only provided for these compounds against *Plasmo-*  
20 *para viticola*, a member of the oomycete class of fungi.

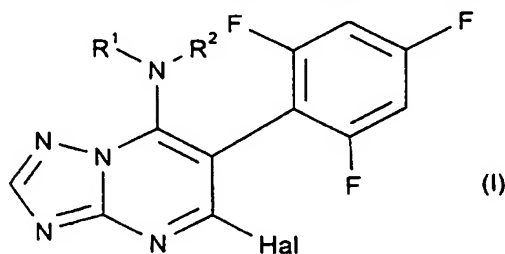
US patent no. 5,593,996 embraces compounds of the general formula



in which R<sup>1</sup> represents an optionally substituted alkyl, alkenyl, alkadienyl, cycloalkyl, bicycloalkyl or heterocyclyl group; R<sup>2</sup> represents a hydrogen atom or an alkyl group; or R<sup>1</sup> and R<sup>2</sup> together with the interjacent nitrogen atom represent an optionally substituted heterocyclic ring; R<sup>3</sup> represents an optionally substituted aryl group; and R<sup>4</sup> represents a hydrogen or halogen atom or a group -NR<sup>5</sup>R<sup>6</sup> where R<sup>5</sup> represents a hydrogen atom or an amino, alkyl, cycloalkyl or bicycloalkyl group and R<sup>6</sup> represents a hydrogen atom or an alkyl group. Thus, compounds in which R<sup>3</sup> is a trifluorophenyl group are generally covered by this patent application. These compounds are said to be active against fungi which are members of the ascomycetes class such as *Venturia inaequalis* and of the hyphomycetes class such as *Alternaria solani* and *Botrytis cinerea*. However, there is no single compound disclosed in which R<sup>3</sup> is a 2,4,6-trifluorophenyl group.

### SUMMARY OF THE INVENTION

5 The present invention provides a compound of formula I



in which

R<sup>1</sup> and R<sup>2</sup> each independently represent a hydrogen atom or an optionally substituted alkyl, alkenyl, alkynyl, alkadienyl, haloalkyl, aryl, heteroaryl,

10 cycloalkyl, bicycloalkyl, tricycloalkyl or heterocyclyl group, or

R<sup>1</sup> and R<sup>2</sup> together with the interjacent nitrogen atom represent an optionally substituted heterocyclic ring,

Hal represents a halogen atom.

the new compounds show an excellent selective fungicidal activity in

15 various crops.

It is an object of the present invention to provide novel, selective fungicidal compounds.

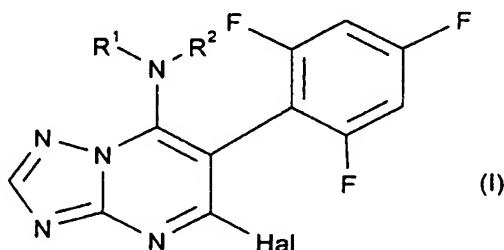
It is also an object of the invention to provide methods for controlling an undesired fungus by contacting said plants with a  
20 fungicidally effective amount of the new compounds.

It is another object of the invention to provide selective fungicidal compositions containing the new compounds as active ingredients.

These and other objects and features of the invention will be more apparent from the detailed description set forth hereinbelow, and from the  
25 appended claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has surprisingly been found that the compounds of formula I



- 5 in which  $R^1$ ,  $R^2$  and Hal have the meaning given above for formula I show an excellent fungicidal activity against a broad range of fungi.

In general terms, unless otherwise stated, as used herein the term halogen atom may denote a bromine, iodine, chlorine or fluorine atom, and is especially a bromine, chlorine or fluorine atom, in particular a chlorine atom.

10 Hal represents preferably a fluorine, chlorine, bromine or iodine atom, in particular a chlorine atom.

Optionally substituted moieties may be unsubstituted or have from one up to the maximal possible number of substituents. Typically, 0 to 2 substituents are present.

15 In general terms, unless otherwise stated herein, the terms alkyl, alkenyl, alkynyl, alkadienyl as used herein with respect to a radical or moiety refer to a straight or branched chain radical or moiety. As a rule, such radicals have up to 10, in particular up to 6 carbon atoms. Suitably an alkyl moiety has from 1 to 6 carbon atoms, preferably from 1 to 3 carbon atoms. A preferred alkyl moiety is an ethyl or especially a methyl group. Suitably an alkenyl moiety has from 2 to 6 carbon atoms. A preferred alkenyl moiety is allyl or especially a 2-methylallyl group.

25 In general terms, unless otherwise stated herein, the term aryl, as used herein with respect to a radical or moiety refers to an aryl group having 6, 10 or 14 carbon atoms, preferably 6 or 10 carbon atoms, in particular phenyl being optionally substituted by one or more halogen

atoms, nitro, cyano, alkyl, preferably C<sub>1-6</sub> alkyl, alkoxy, preferably C<sub>1-6</sub> alkoxy.

In general terms, unless otherwise stated herein, the term heteroaryl, as used herein with respect to a radical or moiety refers to a heteroaryl group having 5 or 6 ring atoms selected from carbon, nitrogen, oxygen and sulphur, at least one of which being nitrogen, oxygen or sulphur.

In general terms, unless otherwise stated herein, the term cycloalkyl, as used herein with respect to a radical or moiety refers to a cycloalkyl group having 3 to 8 carbon atoms, preferably 5 to 7 carbon atoms, in particular cyclohexyl being optionally substituted by one or more halogen atoms, nitro, cyano, alkyl, preferably C<sub>1-6</sub> alkyl, alkoxy, preferably C<sub>1-6</sub> alkoxy.

In general terms, unless otherwise stated herein, the term heterocyclyl, as used herein with respect to a radical or moiety refers to a saturated heterocyclyl group having 5 or 6 ring atoms selected from carbon, nitrogen, oxygen and sulphur, at least one of which being nitrogen, oxygen or sulphur being optionally substituted by one or more halogen atoms, nitro, cyano, alkyl, preferably C<sub>1-6</sub> alkyl, alkoxy, preferably C<sub>1-6</sub> alkoxy, in particular pyrrolodiny, pyrrazolidin, piperidiny, piperaziny or morpholin-4-yl.

The invention especially relates to compounds of the general formula I in which any alkyl part of the groups R<sup>1</sup> or R<sup>2</sup>, which may be straight chained or branched, contains up to 10 carbon atoms, preferably up to 9 carbon atoms, more preferably up to 6 carbon atoms, any alkenyl or alkynyl part of the substituents R<sup>1</sup> or R<sup>2</sup> contains up to 10 carbon atoms, preferably up to 9 carbon atoms, more preferably up to 6 carbon atoms, any cycloalkyl part of the substituents R<sup>1</sup> or R<sup>2</sup> contains from 3 to 10 carbon atoms, preferably from 3 to 8 carbon atoms, more preferably from 3 to 6 carbon atoms, and any aryl part of the substituent R<sup>1</sup> or R<sup>2</sup> contains 6, 10 or 14 carbon atoms, preferably 6 or 10 carbon atoms, and in which each optionally substituted group independently is substituted by

one or more halogen atoms or nitro, cyano, hydroxy, alkyl, preferably C<sub>1-6</sub> alkyl, cycloalkyl, preferably C<sub>3-6</sub> cycloalkyl, cycloalkenyl, preferably C<sub>3-6</sub> cycloalkenyl, haloalkyl, preferably C<sub>1-6</sub> haloalkyl, halocycloalkyl, preferably C<sub>3-6</sub> halocycloalkyl, alkoxy, preferably C<sub>1-6</sub> alkoxy, haloalkoxy, preferably C<sub>1-6</sub> haloalkoxy, trialkylsilyl, preferably tri-C<sub>1-4</sub> alkylsilyl, phenyl, halo- or dihalo-phenyl or pyridyl groups. Any alkyl, alkenyl or alkynyl group may be linear or branched. A 4- to 6- membered heterocyclic group may be any heterocyclic group with 4 to 6 ring atoms, interrupted by one or more heteroatoms selected from sulfur, nitrogen, and oxygen, preferably oxygen. A halogen atom suitably denotes a fluorine, chlorine or bromine atom.

The invention especially relates to compounds of the general formula I in which R<sup>1</sup> represents a straight-chained or branched C<sub>1-10</sub> alkyl, in particular a branched C<sub>3-10</sub> alkyl group, a C<sub>3-8</sub> cycloalkyl, a C<sub>3-8</sub> cycloalkyl-C<sub>1-6</sub> alkyl, C<sub>1-10</sub> alkoxy-C<sub>1-6</sub> alkyl, a C<sub>1-10</sub> haloalkyl or a phenyl group being optionally substituted by one to three halogen atoms or C<sub>1-10</sub> alkyl or C<sub>1-10</sub> alkoxy groups

The invention especially relates to compounds of the general formula I in which R<sup>2</sup> represents a hydrogen atom, a C<sub>1-10</sub> alkyl or a C<sub>1-10</sub> haloalkyl group, in particular a hydrogen atom.

If R<sup>1</sup> denotes a C<sub>1-10</sub> haloalkyl group, preferably a polyfluorinated alkyl group, in particular a 2,2,2-trifluoroethyl, a 2-(1,1,1-trifluoropropyl) or a 2-(1,1,1-trifluorobutyl) group, R<sup>2</sup> preferably represents a hydrogen atom.

If R<sup>1</sup> denotes an optionally substituted C<sub>3-8</sub> cycloalkyl group, preferably a cyclopentyl or cyclohexyl group, R<sup>2</sup> preferably represents a hydrogen atom or C<sub>1-6</sub> alkyl group.

The invention especially relates to compounds of the general formula I in which R<sup>1</sup> and R<sup>2</sup> together with the interjacent nitrogen atom form an optionally substituted heterocyclic ring, preferably an optionally substituted C<sub>3-7</sub> heterocyclic ring, in particular a pyrrolidine, piperidine, tetrahydropyridine, in particular 1,2,3,6-tetrahydropyridine or azepane ring which is optionally substituted by one or more C<sub>1-10</sub> alkyl groups.



Included in the scope of the present invention are (R) and (S) isomers of compounds of general formula I having an chiral center and the racemates thereof, and salts, N-oxides and acid addition compounds.

Particularly interesting activity has been found in (S)-isomer compounds of general formula I wherein R<sup>1</sup> represent a chiral group of formula -CH\*(R')R'', wherein R' and R'' represent different alkyl or haloalkyl groups.

The compounds according to general formula I are oils, gums, or, predominantly crystalline solid materials. They are superior through their valuable fungicidal properties, in particular their enhanced systemicity and enhanced fungicotoxicity against rice diseases and powdery mildews. For example, they can be used in agriculture or related fields for the control of phytopathogenic fungi such as *Alternaria solani*, *Botrytis cinerea*, *Cercospora beticola*, *Cladosporium herbarum*, *Corticium rolfsii*, *Erysiphe graminis*, *Helminthosporium tritici repentis*, *Leptosphaeria nodorum*, *Micronectriella nivalis*, *Monilinia fructigena*, *Mycosphaerella ligulicola*, *Mycosphaerella pinodes*, *Pyricularia grisea f.sp. oryzae*, *Rhizoctonia solani* and *Sclerotinia sclerotiorum*, *Uncinula necator*, in particular for the control of *Uncinula necator*. The compounds of general formula I according to the invention possess a high fungicidal activity within a wide concentration range and may be used in agriculture without any difficulties.

Moreover, the compounds according to the invention show enhanced residual control of fungi, in particular of grape powdery mildew compared with conventional fungicides.

Good results in terms of control of phythopathogenic fungi are obtained with a compound as defined in formula I wherein:

Hal represents a chloro atom, and

R<sup>2</sup> represents a hydrogen atom.

Especially good results in terms of control of phytopathogenic fungi are obtained by using, for example, the following compounds of formula I:

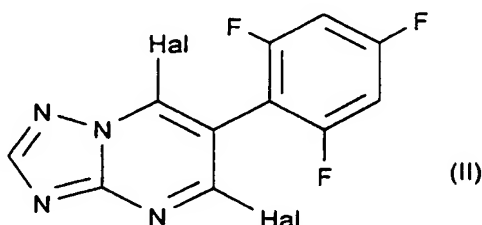
- 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N,N-diethylamino)-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-ethyl-N-2-  
methylallylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine,  
5 5-chloro-7-(2-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-isopropylamino)-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-  
cyclopentylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine,  
5-chloro-7-(N-but-2-ylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
10 pyrimidine, 5-chloro-7-(thiomorpholino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(azepan-1-yl)-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-allyl-N-  
ethylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-  
chloro-7-(N-norborn-2-ylamino)-6-(2,4,6-trifluorophenyl)-  
15 [1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(8-aza-1,5-  
dioxaspiro[5.5]undecan-8-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
pyrimidine, 5-chloro-7-(N-2,2,2-trifluoroethylamino)-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(1,2,5,6-  
tetrahydropyrid-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
20 pyrimidine, 5-chloro-7-(N-2-methylpropylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine; 5-chloro-7-(N-methyl-N-2-allylamino)-6-  
(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine; 5-chloro-7-(N-  
ethylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine; 5-  
chloro-7-(N-1,2,2-trimethylpropylamino)-6-(2,4,6-trifluorophenyl)-  
25 [1,2,4]triazolo[1,5-a]pyrimidine; 5-chloro-7-(N-ethyl-N-isopropylamino)-6-  
(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-allyl-  
N-1-methylpropylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
pyrimidine, 5-chloro-7-(N-1,2-dimethylpropylamino)-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-isopropyl-N-  
30 2-methylpropylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
pyrimidine, 5-chloro-7-(N-2-methylpropyl-N-1-methylpropylamino)-6-  
(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-2-

- methylpropyl-N-2,2,2-trifluoroethylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-methyl-N-2,2,2-  
trifluoroethylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
pyrimidine, 5-chloro-7-[N-2-(1,1,1-trifluoropropyl)-amino]-6-(2,4,6-  
5 trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-1-  
phenylethyl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-  
chloro-7-(N-ethyl-N-2-methylpropylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-but-2-yl-N-methylamino)-6-  
(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-  
10 cyclopentyl-N-methylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
pyrimidine, 5-chloro-7-[N-(2,2,2-trifluoroethyl)-N-(trimethylsilylmethyl)-  
amino]-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-  
(3-hydroxypiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
pyrimidine, 5-chloro-7-(3-hydroxypyrrolidin-1-yl)-6-(2,4,6-trifluorophenyl)-  
15 [1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-[N-(2-(3-fluorophenyl)-ethyl)-  
amino]-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-  
[N-(1-(4-methylphenyl)-ethyl)-amino]-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-4-*tert*-butylcyclohexyl-  
amino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-  
20 (tetrahydropyrid-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
pyrimidine, 5-chloro-7-(1,2,3,6-tetrahydropyrid-1-yl)-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-2-  
hydroxypropylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
pyrimidine, 5-chloro-7-(4-hydroxypiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-  
25 [1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(4-hydroxymethylpiperidin-1-yl)-  
6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-[N-(1-  
phenyl-2,2,2-trifluoroethyl)-amino]-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-[N-2-(1,1,1-trifluorobutyl)-  
amino]-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-  
30 [N-(3-methylbutyl)-N-methylamino]-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-[N-2-(3-methyl-1,1,1-  
trifluorobutyl)-amino]-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-

- pyrimidine, 5-chloro-7-(1,1,3,3-tetramethylbutylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-[3-(2-methylhexyl)-amino]-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
 5 pyrimidine, 5-chloro-7-[2-(5-methylhexyl)-amino]-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 5-chloro-7-(N-3-chloro-tricyclo[2.2.1.0<sup>2,6</sup>]hept-5-ylaminio)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine.

The present invention further provides a process for the preparation of a compound of formula I as defined above which comprises

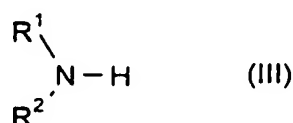
- 10 treating a compound of the general formula II



in which

Hal is as defined for formula I;

with an amine of the general formula III



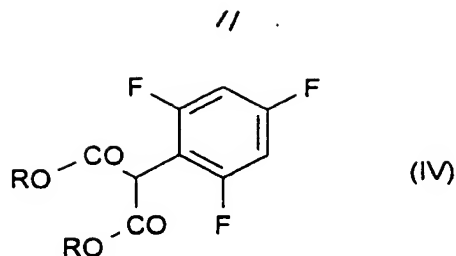
15

in which

R<sup>1</sup> and R<sup>2</sup> are as defined for formula I,

to produce a compound of formula I

- Compounds of formula II are novel and are conventionally  
 20 prepared by reacting 3-amino-1,2,4-triazole with 2-(2,4,6-trifluorophenyl)-substituted malonic acid ester of formula IV,



wherein R represents alkyl, preferably C<sub>1-6</sub> alkyl, in particular methyl or ethyl, under alkaline conditions, preferably using high boiling tertiary amines as for example tri-n-butylamine.

5           The resulting 5,7-dihydroxy-6-(2,4,6-trifluorophenyl)-triazolopyrimidine is subsequently treated with a halogenating agent, preferably with a brominating or chlorinating agent, such as phosphorus oxybromide or phosphorus oxychloride, neat or in the presence of a solvent. The reaction is suitably carried out at a temperature in the range  
10   from 0 °C to 150 °C, the preferred reaction temperature being from 80 °C to 125 °C.

Accordingly, the invention relates to the novel intermediates of formula II, in particular 5,7-dichloro-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, and formula IV and to the novel 5,7-  
15   dihydroxy-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine.

The reaction between the 5,7-dihalo-6-(2,4,6-trifluorophenyl)-triazolopyrimidines of formula II and the amine of formula III is preferably carried out in the presence of a solvent. Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran,  
20   halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example toluene. The reaction is suitably carried out at a temperature in the range from 0 °C to 70 °C, the preferred reaction temperature being from 10 °C to 35 °C. It is also preferred that the reaction is carried out in the presence of a base. Suitable bases include  
25   tertiary amines, such as triethylamine, and inorganic bases, such as potassium carbonate or sodium carbonate. Alternatively, an excess of the compound of formula III may serve as a base.

Due to excellent activity, the compounds of formula I may be used in cultivation of all plants where infection by phytopathogenic fungi is not

desired, e.g. cereals, solanaceous crops, vegetables, legumes, apples, vine.

The compounds of general formula I have been found to have fungicidal activity. Accordingly, the invention further provides a fungicidal composition which comprises an active ingredient, which is at least one compound of formula I as defined above, and one or more carriers. A method of making such a composition is also provided which comprises bringing a compound of formula I as defined above into association with the carrier(s). Such a composition may contain a single active ingredient or a mixture of several active ingredients of the present invention. It is also envisaged that different isomers or mixtures of isomers may have different levels or spectra of activity and thus compositions may comprise individual isomers or mixtures of isomers.

A composition according to the invention preferably contains from 0.5% to 95% by weight (w/w) of active ingredient.

A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for example be a plant, seed, soil, or water in which a plant grows, or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including material which is normally a gas but which has been compressed to form a liquid.

The compositions may be manufactured into e.g. emulsion concentrates, solutions, oil in water emulsions, wettable powders, soluble powders, suspension concentrates, dusts, granules, water dispersible granules, micro-capsules, gels, tablets and other formulation types by well-established procedures. These procedures include intensive mixing and/or milling of the active ingredients with other substances, such as fillers, solvents, solid carriers, surface active compounds (surfactants), and optionally solid and/or liquid auxiliaries and/or adjuvants. The form of application such as spraying, atomizing, dispersing or pouring may be chosen like the compositions according to the desired objectives and the given circumstances.

Solvents may be aromatic hydrocarbons, e.g. Solvesso<sup>®</sup> 200, substituted naphthalenes, phthalic acid esters, such as dibutyl or dioctyl phthalate, aliphatic hydrocarbons, e.g. cyclohexane or paraffins, alcohols and glycols as well as their ethers and esters, e.g. ethanol, ethyleneglycol mono- and dimethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, or  $\gamma$ -butyrolactone, higher alkyl pyrrolidones, e.g. n-octylpyrrolidone or cyclohexylpyrrolidone, epoxidized plant oil esters, e.g. methylated coconut or soybean oil ester and water. Mixtures of different liquids are often suitable.

Solid carriers, which may be used for dusts, wettable powders, water dispersible granules, or granules, may be mineral fillers, such as calcite, talc, kaolin, montmorillonite or attapulgite. The physical properties may be improved by addition of highly dispersed silica gel or polymers. Carriers for granules may be porous material, e.g. pumice, kaolin, sepiolite, bentonite; non-sorptive carriers may be calcite or sand. Additionally, a multitude of pre-granulated inorganic or organic materials may be used, such as dolomite or crushed plant residues.

Pesticidal compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a carrier which is a surfactant facilitates this process of dilution. Thus, preferably at least one carrier in a composition according to the invention is a surfactant. For example, the composition may contain at two or more carriers, at least one of which is a surfactant.

Surfactants may be nonionic, anionic, cationic or zwitterionic substances with good dispersing, emulsifying and wetting properties depending on the nature of the compound according to general formula I to be formulated. Surfactants may also mean mixtures of individual surfactants.

The compositions of the invention may for example be formulated as wettable powders, water dispersible granules, dusts, granules, tablets, solutions, emulsifiable concentrates, emulsions, suspension concentrates

and aerosols. Wettable powders usually contain 5 to 90% w/w of active ingredient and usually contain in addition to solid inert carrier, 3 to 10% w/w of dispersing and wetting agents and, where necessary, 0 to 10% w/w of stabilizer(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and may be diluted in the field with further solid carrier to give a composition usually containing 0.5 to 10% w/w of active ingredient. Water dispersible granules and granules are usually prepared to have a size between 0.15 mm and 2.0 mm and may be manufactured by a variety of techniques. Generally, these types of granules will contain 0.5 to 90% w/w active ingredient and 0 to 20% w/w of additives such as stabilizer, surfactants, slow release modifiers and binding agents. The so-called "dry flowables" consist of relatively small granules having a relatively high concentration of active ingredient.

Emulsifiable concentrates usually contain, in addition to a solvent or a mixture of solvents, 1 to 80% w/v active ingredient, 2 to 20% w/v emulsifiers and 0 to 20% w/v of other additives such as stabilizers, penetrants and corrosion inhibitors. Suspension concentrates are usually milled so as to obtain a stable, non-sedimenting flowable product and usually contain 5 to 75% w/v active ingredient, 0.5 to 15% w/v of dispersing agents, 0.1 to 10% w/v of suspending agents such as protective colloids and thixotropic agents, 0 to 10% w/v of other additives such as defoamers, corrosion inhibitors, stabilizers, penetrants and stickers, and water or an organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation and crystallization or as antifreeze agents for water.

Aqueous dispersions and emulsions, for example compositions obtained by diluting the formulated product according to the invention with water, also lie within the scope of the invention.

Of particular interest in enhancing the duration of the protective activity of the compounds of this invention is the use of a carrier which will provide



slow release of the pesticidal compounds into the environment of a plant which is to be protected.

The biological activity of the active ingredient can also be increased by including an adjuvant in the spray dilution. An adjuvant is defined here as a substance which can increase the biological activity of an active ingredient but is not itself significantly biologically active. The adjuvant can either be included in the formulation as a coformulant or carrier, or can be added to the spray tank together with the formulation containing the active ingredient.

As a commodity the compositions may preferably be in a concentrated form whereas the end user generally employs diluted compositions. The compositions may be diluted to a concentration down to 0.001% of active ingredient. The doses usually are in the range from 0.01 to 10 kg a.i./ha.

Examples of formulations according to the invention are:

#### Emulsion Concentrate (EC)

Active Ingredient	Compound of Example 2	30 % (w/v)
Emulsifier(s)	Atlox® 4856 B / Atlox® 4858 B <sup>1)</sup> (mixture containing calcium alkyl aryl sulfonate, fatty alcohol ethoxylates and light aromatics / mixture containing calcium alkyl aryl sulfonate, fatty alcohol ethoxylates and light aromatics)	5 % (w/v)
Solvent	Shellsol® A <sup>2)</sup> (mixture of C <sub>9</sub> - C <sub>10</sub> aromatic hydrocarbons)	to 1000 ml

#### Suspension Concentrate (SC)

Active Ingredient	Compound of Example 2	50 % (w/v)
Dispersing agent	Soprophor® FL <sup>3)</sup> (polyoxyethylene polyaryl phenyl ether phosphate amine salt)	3 % (w/v)
Antifoaming agent	Rhodorsil® 422 <sup>3)</sup> (nonionic aqueous emulsion of polydimethylsiloxanes)	0.2 % (w/v)

Structure agent	Kelzan® S <sup>4)</sup>	0.2 %
	(Xanthan gum)	(w/v)
Antifreezing agent	Propylene glycol	5 % (w/v)
Biocidal agent	Proxel® <sup>5)</sup>	0.1 %
	(aqueous dipropylene glycol solution containing 20% 1,2-benisoctiazolin-3-one)	(w/v)

Water to 1000 ml

Wettable Powder (WP)

Active Ingredient	Compound of Example 2	60 % (w/w)
Wetting agent	Atlox® 4995 <sup>1)</sup>	2 % (w/w)
	(polyoxyethylene alkyl ether)	
Dispersing agent	Witcosperse® D-60 <sup>6)</sup>	3 % (w/w)
	(mixture of sodium salts of condensed naphthalene sulfonic acid and alkylaryl polyoxy acetates)	
Carrier / Filler	Kaolin	35 % (w/w)

Water Dispersible Granules (WG)

Active Ingredient	Compound of Example 2	50 % (w/w)
Dispersing /	Witcosperse® D-450 <sup>6)</sup>	8 % (w/w)
Binding agent	(mixture of sodium salts of condensed naphthalene sulfonic acid and alkyl sulfonates)	
Wetting agent	Morwet® EFW <sup>6)</sup>	2 % (w/w)
	(formaldehyde condensation product)	
Antifoaming agent	Rhodorsil® EP 6703 <sup>3)</sup>	1 % (w/w)
	(encapsulated silicone)	
Disintegrant	Agrimer® ATF <sup>7)</sup>	2 % (w/w)
	(cross-linked homopolymer of N-vinyl-2- pyrrolidone)	
Carrier / Filler	Kaolin	35 % (w/w)

1) commercially available from ICI Surfactants

2) commercially available from Deutsche Shell AG

- 3) commercially available from Rhône-Poulenc
- 4) commercially available from Kelco Co.
- 5) commercially available from Zeneca
- 6) commercially available from Witco
- 5 7) commercially available from International Speciality Products

The compositions of this invention can also comprise other compounds having biological activity, e.g. compounds having similar or complementary pesticidal activity or compounds having plant growth  
10 regulating, fungicidal or insecticidal activity. These mixtures of pesticides can have a broader spectrum of activity than the compound of general formula I alone. Furthermore, the other pesticide can have a synergistic effect on the pesticidal activity of the compound of general formula I.

The other fungicidal compound can be, for example, one which is  
15 also capable of combating diseases of cereals (e.g. wheat) such as those caused by *Erysipha*, *Puccinia*, *Septoria*, *Gibberella* and *Helminthosporium* spp., seed and soil borne diseases and downy and powdery mildews on vines, early and late blight on solanaceous crops, and powdery mildew and scab on apples etc. These mixtures of fungicides can have a broader  
20 spectrum of activity than the compound of general formula I alone. Furthermore, the other fungicide can have a synergistic effect on the fungicidal activities of the compound of general formula I.

Examples of the other fungicidal compounds are anilazine, azoxystrobin, benalaxyl, benomyl, bethoxazin, binapacryl, bitertanol, blastidicin S, Bordeaux mixture, bromuconazole, bupirimate, captafol, captan, carbendazim, carboxin, carpropamid, chlorbenzthiazon, chlorothalonil, chlozolinatate, copper-containing compounds such as copper  
25 oxychloride, and copper sulfate, cycloheximide, cymoxanil, cypofuram, cyproconazole, cyprodinil, dichlofluanid, dichlone, dichloran, diclobutrazol, diclocymet, diclomezine, diethofencarb, difenoconazole, diflumetorim,  
30 dimethirimol, dimethomorph, diniconazole, dinocap, ditalimfos, dithianon, dodemorph, dodine, edifenphos, epoxiconazole, etaconazole, ethirimol, etridiazole, famoxadone, fenapanil, fenarimol, fenbuconazole, fenfuram,

fenhexamid, fenpiclonil, fenpropidin, fenpropimorph, fentin, fentin acetate, fentin hydroxide, ferimzone, fluazinam, fludioxonil, flumetover, fluquinconazole, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetyl-aluminium, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole, 5 imazalil, iminoctadine, ipconazole, iprodione, isoprothiolane, kasugamycin, kitazin P, kresoxim-methyl, mancozeb, maneb, mepanipyrin, mepronil, metalaxyl, metconazole, methfuroxam, myclobutanil, neoasozin, nickel dimethyldithiocarbamate, nitrothalisopropyl, nuarimol, ofurace, organo mercury compounds, 10 oxadixyl, oxycarboxin, penconazole, pencycuron, phenazineoxide, phthalide, polyoxin D, polyram, probenazole, prochloraz, procymidione, propamocarb, propiconazole, propineb, pyrazophos, pyrifenoxy, pyrimethanil, pyroquilon, pyroxyfur, quinomethionate, quinoxifen, quintozone, spiroxamine, SSF-126, SSF-129, streptomycin, sulfur, 15 tebuconazole, tecloftalame, tecnazene, tetraconazole, thiabendazole, thifluzamide, thiophanate-methyl, thiram, tolclofosmethyl, tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, tricyclazole, tridemorph, triflumizole, triforine, triticonazole, validamycin A, vinclozolin, XRD-563, zarilamid, zineb, ziram

20 In addition, the co-formulations according to the invention may contain at least one compound of formula I and any of the following classes of biological control agents such as viruses, bacteria, nematodes, fungi, and other microorganisms which are suitable to control insects, weeds or plant diseases or to induce host resistance in the plants.

25 Examples of such biological control agents are: *Bacillus thuringiensis*, *Verticillium lecanii*, *Autographica californica* NPV, *Beauveria bassiana*, *Ampelomyces quisqualis*, *Bacillus subtilis*, *Pseudomonas chlororaphis*, *Pseudomonas fluorescens*, *Streptomyces griseoviridis* and *Trichoderma harzianum*.

30 Moreover, the co-formulations according to the invention may contain at least one compound of formula I and a chemical agent that

induces the systemic acquired resistance in plants such as for example nicotinic acid or derivatives thereof or BION.

The compounds of general formula I can be mixed with soil, peat or other rooting media for the protection of the plants against seed-borne, soil-borne or foliar fungal diseases.

The invention still further provides the use as a fungicide of a compound of the general formula I as defined above or a composition as defined above, and a method for combating fungus at a locus, which comprises treating the locus, which may be for example plants subject to or subjected to fungal attack, seeds of such plants or the medium in which such plants are growing or are to be grown, with such a compound or composition.

The present invention is of wide applicability in the protection of crop and ornamental plants against fungal attack. Typical crops which may be protected include vines, grain crops such as wheat and barley, rice, sugar beet, top fruit, peanuts, potatoes, vegetables and tomatoes. The duration of the protection is normally dependent on the individual compound selected, and also a variety of external factors, such as climate, whose impact is normally mitigated by the use of a suitable formulation.

The following examples further illustrate the present invention. It should be understood, however, that the invention is not limited solely to the particular examples given below.

#### **Example 1**

5-Chloro-(2,4,6-trifluorophenyl)-7-(N,N-diethylamino)-1,2,4-triazolo[1.5a]pyrimidine

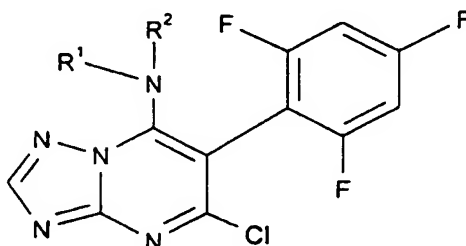
A mixture of N,N-diethylamine (1.4 mmoles), triethylamine (1.4 mmoles) and dichloromethane (10 ml) is added to a mixture of 5,7-dichloro-(2,4,6-trifluorophenyl)-1,2,4-triazolo[1.5a]pyrimidine (1.4 mmoles) and dichloromethane (30 ml) under stirring. The reaction mixture is stirred 16 hours at room temperature, subsequently washed two times with 1 N hydrochloric acid and once with water. The organic layer is separated,

dried with anhydrous sodium sulphate and the solvent is evaporated under reduced pressure. Treatment of the resulting light brown oil with *tert.*-butyl methyl ether (50 ml) yields beige crystals (79% of theory) having a melting point of 118 °C.

5

### Examples 2-60

The following examples (Table I; structure and melting point) are synthesized analogously to Example 1.



Example	R <sup>1</sup>	R <sup>2</sup>	melting point (° C)
2	-(CH <sub>2</sub> ) <sub>2</sub> -CH(CH <sub>3</sub> )-(CH <sub>2</sub> ) <sub>2</sub> -		155
3	2-methylallyl	ethyl	91-93
4	-CH(CH <sub>3</sub> )-(CH <sub>2</sub> ) <sub>4</sub> -		118-119
5	iso-propyl	H	foam
6	cyclopentyl	H	foam
7	2-butyl	H	56
8	-(CH <sub>2</sub> ) <sub>2</sub> -S-(CH <sub>2</sub> ) <sub>2</sub> -		154-156
9	-(CH <sub>2</sub> ) <sub>6</sub> -		109
10	allyl	ethyl	93-94
11	norbornyl	H	foam
12	2,2,2-trifluoroethyl	H	195
13	-CH <sub>2</sub> -CH=CH-(CH <sub>2</sub> ) <sub>2</sub> -		155
14	but-2-yl	H	91
15	1-methylpropyl	H	117
16	2-methylallyl	methyl	170-171
17	ethyl	H	oil

18	1,2,2-trimethylpropyl	H	131
19	2,2,2-trifluoroethyl	allyl	104-105
20	2,2,2-trifluoroethyl	ethyl	133-134
21	isopropyl	ethyl	141
22	2-methylpropyl	allyl	96
23	1,2-dimethylpropyl	H	109
24	isopropyl	H	196
25	2-methylpropyl	methyl	105
26	2,2,2-trifluoroethyl	2-methylpropyl	133-134
27	2,2,2-trifluoroethyl	methyl	163
28	2-(1,1,1-trifluoropropyl)	H	184-185
29	2,2,2-trifluoroethyl	isopropyl	154-158
30	1-phenylethyl	H	172
31	2-methylpropyl	ethyl	87-91
32	cyclopentyl	methyl	142
33	but-2-yl	methyl	161
34	2,2,2-trifluoroethyl	2,2,2-trifluoroethyl	177-179
35	trimethylsilylmethyl	H	148-150
36	1,4-dimethylpentyl	H	124-125
37	1,2-dimethylpropyl	methyl	131-133
38	1-methylbutyl	H	oil
39	cyclopentyl	methyl	142
40	trimethylsilylmethyl	2,2,2-trifluoroethyl	85
41	-CH <sub>2</sub> -CH(OH)-(CH <sub>2</sub> ) <sub>3</sub> -		90
42	-CH <sub>2</sub> -CH(OH)-(CH <sub>2</sub> ) <sub>2</sub> -		168-169
43	2-(3-F-C <sub>6</sub> H <sub>4</sub> )-ethyl	H	162
44	1-(4-methyl-C <sub>6</sub> H <sub>4</sub> )-ethyl	H	62
45	4- <i>tert</i> -butylcyclohexyl	H	200
46	-CH=CH-(CH <sub>2</sub> ) <sub>3</sub> -		165
47	2-hydroxypropyl	H	167
48	-(CH <sub>2</sub> ) <sub>2</sub> -CH(OH)-(CH <sub>2</sub> ) <sub>2</sub> -		150
49	hex-2-yl	H	oil

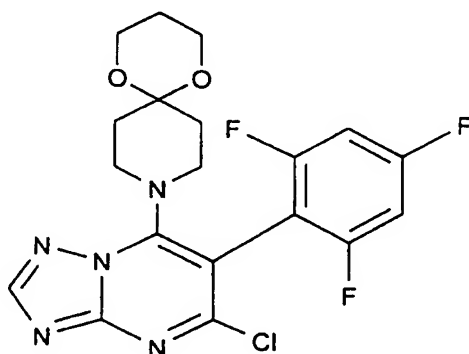
50	-CH <sub>2</sub> -CH=CH-(CH <sub>2</sub> ) <sub>2</sub> -		154
51	-(CH <sub>2</sub> ) <sub>2</sub> -CH(CH <sub>2</sub> OH)-(CH <sub>2</sub> ) <sub>2</sub> -		193
52	1-(C <sub>6</sub> H <sub>5</sub> )-2,2,2-trifluoroethyl	H	86
53	2-(1,1,1-trifluorobutyl)	H	177
54	3-methylbutyl	methyl	77
55	2-(3-methyl-1,1,1-trifluorobutyl)	H	104
56	1,1,3,3-tetramethylbutyl	H	128
57	3-(2-methylhexyl)	H	79
58	2-(5-methylhexyl)	H	125
59	-(CH <sub>2</sub> ) <sub>4</sub> -		134
60	methyl	methyl	194

**Examples 61 and 62:**

The following examples (Table II; structure and melting point) are synthesized analogously to Example 1.

**Example****Structure****melting point  
(°C)**

61

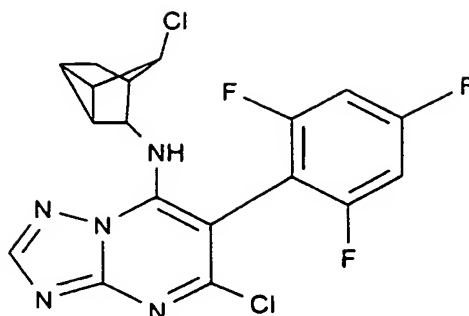


224-225 °C



62

193



### Biological Investigations

#### A. Determination of Minimum Inhibitory Concentration by Test Compounds in the Serial Dilution Test with Various Phytopathogenic Fungi

5        The MIC (Minimum Inhibitory Concentration) value, which indicates the lowest concentration of the active ingredient in the growth medium which causes a total inhibition of mycelial growth, is determined by serial dilution tests using Microtiter plates with 24 or 48 wells per plate. The dilution of the test compounds in the nutrient solution and the distribution

10    to the wells is carried out by a TECAN RSP 5000 Robotic Sample Processor. The following test compound concentrations are used: 0.05, 0.10, 0.20, 0.39, 0.78, 1.56, 3.13, 6.25, 12.50, 25.00, 50.00 and 100.00 mg/ml. For preparation of the nutrient solution, V8 vegetable juice (333 ml) is mixed with calcium carbonate (4.95 g), centrifuged, the

15    supernatant (200 ml) diluted with water (800 ml) and autoclaved at 121 °C for 30 min.

      The respective inocula (*Alternaria solani*, ALTESO; *Botrytis cinerea*, BOTRCI; *Leptosphaeria nodorum*, LEPTNO; *Phytophthora infestans*, PHYTIN; *Magnaporthe grisea f. sp. Oryzae*, PYRIOR;

20    *Pyrenophora teres*, PYRNTE; *Rhizoctonia solani*, RHIZSO;) are added into the wells as spore suspensions (50 ml;  $5 \times 10^5$ /ml) or agar slices (6 mm) of an agar culture of the fungus.

      After 6-12 days incubation at suitable temperatures (18-25°C), the MIC values are determined by visual inspection of the plates (Table II; n. t. = not tested).

25    = not tested).

Table II

Ex. No.	ALTESO	BOTRCI	LEPTNO	PHYTIN	PYRIOR	PYRNTE	RHISZO
2	0.04	0.1	6.25	100	0.04	0.2	n. t.
5	0.78	3.13	25	100	0.39	12.5	6.25
12	1.56	1.56	6.25	25	0.2	6.25	6.25
28	0.78	3.13	3.13	110	0.78	6.25	3.13
19	0.39	0.78	3.13	110	0.04	3.13	0.78
20	0.78	0.78	3.13	110	0.04	1.56	0.78
26	0.2	0.2	0.39	110	0.04	110	3.13
27	0.78	3.13	50	110	0.1	12.5	1.56
28	0.78	3.13	3.13	110	0.78	6.25	3.13
39	0.2	3.13	3.13	110	0.78	1.56	6.25
40	0.78	6.25	110	25	1.56	25	110
41	6.25	100	50	110	12.5	25	110
46	1.56	6.25	6.25	110	1.56	12.5	3.13
49	0.78	3.13	6.25	110	1.56	1.56	50
50	0.39	3.13	1.56	110	0.2	3.13	1.56
52	3.13	12.5	110	110	1.56	3.13	110
54	0.78	3.13	12.5	110	0.04	3.13	110
55	0.39	1.56	1.56	100	0.04	6.25	12.5
57	0.2	0.39	0.78	110	0.04	3.13	110

**B. Method for Evaluation of the compounds of formula I to control**  
 5 powdery mildew on grapes (*Uncinula necator*)

**Test plants**

Cuttings of cultivar Müller-Thurgau were grown in the greenhouse at temperatures between 18 °C and 25 °C and 50 to 70 % relative humidity.

When 6 to 8 leaves had developed the plants were cut back to 3 - 4

equally sized leaves. Plants were cultivated in pots containing FLORAGAD as a substrate.

#### Application

Three to four plants per treatment were used. Application of the compounds of formula I was carried out 3 days before infection in the prophylactic tests. The test plants were sprayed to run off in a spray cabinet using 20 ml of spray wash. The compounds of formula I were dissolved in acetone at a concentration of 0.5 %. The stock solution was diluted with water to give final the concentrations. Formulated fungicides were also diluted with water prior to application.

#### Infection

The plants were artificially infected with conidia of *Uncinula necator* by dusting spores from freshly sporulating grape leaves from the *Uncinula necator* stock culture over the test plants. The spores were allowed to settle on the leaves for 1 hour. The plants remained in the greenhouse without additional light at temperatures between 16 °C and 30 °C for 24 hours.

#### Evaluation

Evaluation was carried out 21 days after infection by assessing the percentage of infected leaf area of each of the 4 treated leaves. The activity in % was calculated using the ABBOTT formula:

$$\% \text{ activity} = 100 - \frac{\% \text{ infection in treated}}{\% \text{ infection in untreated}} \times 100$$

The results of this evaluation are shown in Table II:

Table II

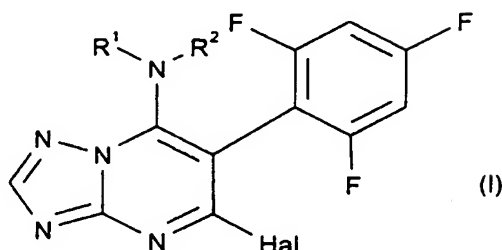
Ex. No.	Concentration [ppm]			
	25.00	12.50	6.25	3.13
2	100	100	100	100
5	100	100	100	100
11	100	100	93	64
12	100	100	100	97
14	100	100	98	86
19	36	34	9	4
20	22	4	0	0
26	27	22	14	0
27	17	11	0	0
28	100	100	100	97
standard <sup>1</sup>	73	44	42	31
Penconazole	58	31	17	11
Fenarimol	99	95	75	31

5-chloro-7-(4-methylpiperidin-1-yl)-6-(2-chloro-6-fluorophenyl)-  
5 [1,2,4]triazolo[1,5-a]pyrimidine which is disclosed in US patent no.  
5,593,996 has been used as standard<sup>1</sup>.

33351

What is claimed is:

1. A compound of the general formula I



in which

R<sup>1</sup> and R<sup>2</sup> each independently represent a hydrogen atom or an optionally substituted alkyl, alkenyl, alkynyl, alkadienyl, haloalkyl, aryl, heteroaryl, cycloalkyl, bicycloalkyl or heterocyclyl group, or

R<sup>1</sup> and R<sup>2</sup> together with the interjacent nitrogen atom represent an optionally substituted heterocyclic ring, and

Hal represents a halogen atom.

2. A compound according to Claim 1 in which

R<sup>1</sup> represents straight chained or branched C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-haloalkyl or straight chained or branched C<sub>2</sub>-C<sub>6</sub>-alkenyl, and R<sup>2</sup> represents hydrogen or C<sub>1</sub>-C<sub>6</sub>-alkyl, or

R<sup>1</sup> and R<sup>2</sup> together with the interjacent nitrogen atom represent a heterocyclic ring with 5 or 6 carbon atoms being optionally substituted with one or two C<sub>1</sub>-C<sub>6</sub>-alkyl groups.

3. A compound according to Claim 1 or 2 in which R<sup>2</sup> represents a hydrogen atom.

4. A compound according to Claim 1 or 2 in which

R<sup>1</sup> and R<sup>2</sup> together with the interjacent nitrogen atom represent a heterocyclic ring selected from 4-methylpiperidin-1-yl, 2-methylpiperidin-1-yl, 5,6-dihydro-2H-pyridin-1-yl, 2-ethylpiperidin-1-yl and azepan-1-yl.

5. The following compounds of formula I:

5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N,N-diethylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-ethyl-N-2-methylallylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(2-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-isopropylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-cyclopentylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-but-2-ylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(4-thiomorpholino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(azepan-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]-  
pyrimidine

5-chloro-7-(N-allyl-N-ethylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-norborn-2-ylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(8-aza-1,5-dioxaspiro[5.5]undecan-8-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-(N-2,2,2-trifluoroethylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-(1,2,5,6-tetrahydropyrid-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-(N-2-methylpropylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-(N-methyl-N-2-methylallylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-(N-ethylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-(N-1,2,2-trimethylpropylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-(N-ethyl-N-isopropylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-(N-allyl-N-2-methylpropylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-(N-1,2-dimethylpropylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-(N-isopropyl-N-2-methylpropylamino)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-[N,N-di-(2-methylpropylamino)]-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-{N-2-methylpropyl-N-[2-(1,1,1-trifluoropropyl)-amino]}-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-{N-methyl-N-[2-(1,1,1-trifluoropropyl)-amino]}-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine

5-chloro-7-[N-2-(1,1,1-trifluoropropyl)-amino]-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-1-phenylethyl)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-ethyl-N-2-methylpropylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-but-2-yl-N-methylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-cyclopentyl-N-methylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-[N-(2,2,2-trifluoroethyl)-N-(trimethylsilylmethyl)-amino]-6-  
(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(3-hydroxypiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(3-hydroxypyrrolidin-1-yl)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-[N-(2-(3-fluorophenyl)-ethyl)-amino]-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-[N-(1-(4-methylphenyl)-ethyl)-amino]-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-4-*tert*-butylcyclohexyl-amino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(tetrahydropyrid-1-yl)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(1,2,3,6-tetrahydropyrid-1-yl)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-2-hydroxypropylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine



5-chloro-7-(4-hydroxypiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(4-hydroxymethylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-[N-(1-phenyl-2,2,2-trifluoroethyl)-amino]-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-[N-2-(1,1,1-trifluorobutyl)-amino]-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-[N-(3-methylbutyl)-N-methylamino]-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-[N-2-(3-methyl-1,1,1-trifluorobutyl)-amino]-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine

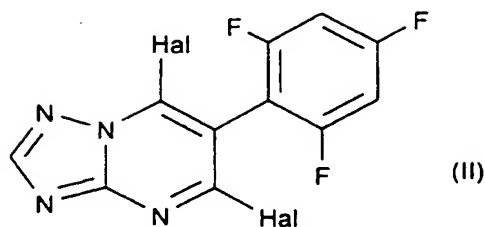
5-chloro-7-(1,1,3,3-tetramethylbutylamino)-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-[3-(2-methylhexyl)-amino]-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-[2-(5-methylhexyl)-amino]-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine

5-chloro-7-(N-3-chlorotricyclo[2.2.1.0<sup>2,6</sup>]hept-5-ylaminio)-6-(2,4,6-  
trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine

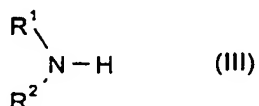
6. A process for the preparation of a compound of formula I  
as defined in claim 1 which comprises  
treating a compound of the general formula II



in which

Hal is as defined in any one of the preceding claims,

with an amine of the general formula III

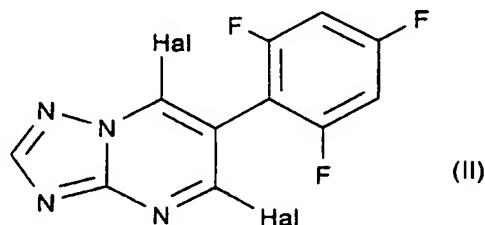


in which

R¹ and R² are as defined in any one of the preceding claims,

to produce a compound of formula I.

7. A compound of formula II



in which

Hal is as defined in any one of the preceding claims.

8. 5,7-Dihydroxy-6-(2,4,6-trifluorophenyl)-  
[1,2,4]triazolo[1,5-a]pyrimidine.

9. A fungicidal composition which comprises a carrier, and as active agent, at least one compound of formula I as defined in any one of Claims 1 to 5.

10. A method of combating fungus at a locus which comprises treating the locus with a compound of formula I as defined in any one of Claims 1 to 5 or with a composition as defined in Claim 9.

11. The use as a fungicide of a compound of formula I as defined in any one of Claims 1 to 5 or a composition as defined in Claim 9.

# INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/US 98/05614

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D487/04 A01N43/90 //(C07D487/04,249:00,239:00)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 593 996 A (K.-J. PEES ET AL.) 14 January 1997 cited in the application see column 6, line 18 - line 33 see claims 1,5,7,11	1,7-11
A	see column 4, line 52 - column 5, line 22 ---	6
Y	EP 0 071 792 A (BASF AG) 16 February 1983 cited in the application see claims 1,2,4,5,8 ---	1,9-11
Y	WO 94 20501 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 15 September 1994 cited in the application see claims 1,6,8,11,13 ---	7-11
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"S" document member of the same patent family

Date of the actual completion of the international search

18 June 1998

Date of mailing of the international search report

29/06/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Hass, C

# INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/US 98/05614

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 612 345 A (H.-M. BECHER ET AL.) 18  March 1997  see claims 1,9,10</p> <p>-----</p>	7,9-11

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/05614

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5593996 A	14-01-1997	AT 159256 T AU 667204 B AU 3043592 A BR 9205172 A CA 2086404 A CN 1075144 A,B CN 1141119 A DE 69222746 D DE 69222746 T DK 550113 T EP 0550113 A EP 0782997 A ES 2108727 T IL 104244 A JP 5271234 A NZ 245581 A PL 171579 B RU 2089552 C ZA 9210043 A	15-11-1997 14-03-1996 01-07-1993 06-07-1993 01-07-1993 11-08-1993 29-01-1997 20-11-1997 12-02-1998 09-02-1998 07-07-1993 09-07-1997 01-01-1998 13-07-1997 19-10-1993 26-07-1995 30-05-1997 10-09-1997 28-07-1993
EP 71792 A	16-02-1983	DE 3130633 A AT 11539 T AU 553663 B AU 8665982 A CA 1180329 A CS 226748 B DK 341682 A,B, JP 1634879 C JP 2061955 B JP 58043974 A US 4567263 A ZA 8205498 A	17-02-1983 15-02-1985 24-07-1986 10-02-1983 01-01-1985 16-04-1984 02-02-1983 20-01-1992 21-12-1990 14-03-1983 28-01-1986 27-07-1983
WO 9420501 A	15-09-1994	AT 159722 T AU 690899 B AU 6258094 A BR 9405988 A CA 2157293 A CN 1119015 A CZ 9502233 A	15-11-1997 07-05-1998 26-09-1994 26-12-1995 15-09-1994 20-03-1996 17-01-1996

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/05614

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9420501 A		DE 69406538 D	04-12-1997
		EP 0699200 A	06-03-1996
		HU 73163 A	28-06-1996
		JP 8507505 T	13-08-1996
		NZ 262729 A	26-01-1996
		PL 310467 A	11-12-1995
		SK 106895 A	05-06-1996
		ZA 9401485 A	10-11-1994
US 5612345 A	18-03-1997	NONE	